

***REMARKS/ARGUMENTS******The Pending Claims***

Claims 1-30 currently are pending. The pending claims are directed to fumed metal oxide particles and a process for producing the same. Reconsideration of the claims is respectfully requested in view of the remarks herein.

***Summary of the Office Action***

The Office Action sets forth the following rejections:

(a) claims 1-3, 7-10, 13-14, 17-18, 20, and 25-30 under 35 U.S.C. § 103 as allegedly obvious over U.S. Patent 5,340,560 (Rohr et al.) (“the Rohr ‘560 patent”) in view of any one of U.S. Patent 6,565,823 (Hawtof et al.) (“the Hawtof ‘823 patent”), U.S. Patent 6,312,656 (Blackwell et al.) (“the Blackwell ‘656 patent”), and U.S. Patent 4,857,076 (Pearson et al.) (“the Pearson ‘076 patent”);

(b) claims 11 and 12 under 35 U.S.C. § 103 as allegedly obvious over the Rohr ‘560 patent in view of U.S. Patent 5,075,090 (Lewis et al.) (“the Lewis ‘090 patent”) and any one of the Hawtof ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent;

(c) claims 1-6 and 13-24 under 35 U.S.C. § 103 as allegedly obvious over U.S. Patent 6,887,566 (Hung et al.) (“the Hung ‘566 patent”) in view of any one of the Hawtof ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent;

(d) claims 11 and 12 under 35 U.S.C. § 103 as allegedly obvious over the Hung ‘566 patent in view of any one of the Hawtof ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent.

Applicants request reconsideration and withdrawal of these rejections for the reasons set forth below.

*Discussion of the Obviousness Rejections*1. *The Rohr '560 Patent*

The Office Action rejects claims 1-3, 7-10, 13-14, 17-18, 20, and 25-30 as allegedly obvious over the Rohr '560 patent in combination with one of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent.

The process for producing fumed metal oxides defined by rejected claim 1 comprises (a) providing a stream of a liquid feedstock comprising a volatizable non-halogenated metal oxide precursor; (b) providing a stream of a combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock; (c) injecting the stream of the liquid feedstock into the stream of combustion gas to thereby atomize the liquid feedstock and form a reaction mixture comprising the combustion gas and the atomized liquid feedstock; and (d) subjecting the atomized liquid feedstock to a sufficient temperature and residence time in the combustion gas stream for fumed metal oxide particles to form before the combustion gas temperature is reduced below the solidifying temperature of the fumed metal oxide particle. Claims 2-3, 7-10, 13-14, 17-18, and 20 are directly or indirectly dependent on, and therefore include all of the limitations of, claim 1.

For subject matter defined by a claim to be considered obvious, the Office must demonstrate that the differences between the claimed subject matter and the prior art “are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains.” 35 U.S.C. § 103(a); see also *Graham v. John Deere Co.*, 383 U.S. 1, 148 U.S.P.Q. 459 (1966). The ultimate determination of whether an invention is or is not obvious is based on certain factual inquiries including: (1) the scope and content of the prior art, (2) the level of ordinary skill in the prior art, (3) the differences between the claimed invention and the prior art, and (4) objective evidence of nonobviousness. *Graham*, 383 U.S. at 17-18, 148 U.S.P.Q. at 467.

The Office Action acknowledges that the Rohr '560 patent fails to teach providing a stream of combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock (see element (b) of claim 1, which reads: “providing a stream of a combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid

feedstock”). However, the Rohr ‘560 patent also fails to teach that the stream of liquid feedstock is *atomized by injection* into the stream of combustion gas (see element (c) of claim 1, which reads, in relevant part: “injecting the stream of the liquid feedstock into the stream of combustion gas to thereby atomize the liquid feedstock”). The Rohr ‘560 patent discloses production of fumed metal oxide particles, but does not disclose that the liquid feedstock is atomized *by injection* into the stream of combustion gas *prior to* conversion to the fumed metal oxide particles as required by the pending method claims. Contrary to the Office Action’s assertions, none of the Hawtof ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent satisfies the deficiencies of the Rohr ‘560 patent.

The combination of the Rohr ‘560 patent and the Hawtof ‘823 patent fails to render the claimed invention obvious. First, the Hawtof ‘823 patent is directed to a method for making *fused* silica, as distinct from the claimed method of making *fumed* metal oxide particles (see Kirk-Othmer Encyclopedia of Chemical Technology (John Wiley & Sons, Inc., 5th ed.. 2006), vol. 22, pp. 380-386, 400-415, and 439-445 (enclosed herewith)). The production methods, chemical properties, and end-use applications of fused and fumed silica are very different. Accordingly, a person of ordinary skill in the art would not look to fused silica art for guidance regarding fumed silica applications. As such, the Hawtof ‘823 patent is not pertinent art to the claimed invention and cannot properly form the basis of an obviousness rejection.

Second, the Hawtof ‘823 patent does not require that the liquid feedstock is atomized *prior to* combustion. Specifically, the Hawtof ‘823 patent discloses a device for delivering the liquid feedstock “either as a liquid stream or as atomized liquid particles, directly into the flame of burner 10” (col. 7, lines 35-36). Put another way, the liquid feedstock can be injected directly into a flame, where it is converted to the finely divided soot that is consolidated into a body of fused silica glass (see col. 7, lines 8-36; col. 8, lines 9-14; Fig. 2). Accordingly, the Hawtof ‘823 patent does not teach or suggest the benefits of atomization prior to combustion, and, as such, would not motivate a person of ordinary skill in the art to employ a method that involves atomization of the liquid feedstock prior to combustion.

Third, and in any event, the Hawtof ‘823 patent does not teach or suggest elements (b) or (c) of pending claim 1 and its attendant dependent claims. With respect to element (b),

i.e., providing a stream of combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock, the Hawtof '823 patent teaches atomization by a high-velocity flowing "carrier gas" stream, e.g., nitrogen, that is part of a known atomizer apparatus, e.g., a pneumatic atomizer or airblast atomizer (see col. 7, line 51 – col. 8, line 57), followed by introduction of the atomized liquid feedstock into a burner unit, i.e., a flame (see, e.g., col. 8, lines 3-8). However, the Hawtof '823 patent does not teach that the liquid feedstock is atomized by the force of the *combustion gas stream* (see para. 0024 of the specification). Additionally, with respect to element (c), i.e., injecting the stream of the liquid feedstock into the stream of combustion gas to thereby atomize the liquid feedstock, although the Hawtof '823 patent teaches that, optionally, the velocity and kinetic energy of a flowing "carrier gas" can be used to atomize the liquid feedstock (see, e.g., col. 8, lines 41-47), nothing in the Hawtof '823 patent teaches or suggests that the liquid feedstock is *atomized by injection* into that stream of gas, let alone that the liquid feedstock is atomized by injection into the stream of the combustion gas (see para. 0024 of the specification, which indicates that the liquid feedstock can be fed to the nozzle under pressure, which ensures that it exits the nozzle, i.e., is injected into the stream of combustion gas, with sufficient force to atomize the liquid feedstock). Accordingly, the combination of the Rohr '560 patent and the Hawtof '823 patent fails to teach or suggest all of the limitations of the pending claims. For this reason alone, let alone all three reasons discussed herein, the subject matter of the pending claims cannot properly be considered obvious over the combination of the Rohr '560 patent and the Hawtof '823 patent.

The combination of the Rohr '560 patent and the Blackwell '656 patent similarly fails to render the claimed invention obvious. The Blackwell '656 patent is a continuation-in-part of the Hawtof '823 patent, and, like the Hawtof '823 patent, does not require that the liquid feedstock is atomized *prior to* combustion. Specifically, the Blackwell '656 patent discloses a device for delivering the liquid feedstock "either as a liquid stream or as atomized liquid particles directly into the flame of burner 10" (col. 8, lines 10-11). Put another way, the liquid feedstock can be delivered to the combustion means as a liquid stream that has not yet been atomized (see, e.g., col. 8, lines 6-11, 55-60; Fig. 2). Because it does not teach the benefits of atomization prior to combustion, the Blackwell '656 patent would not motivate a person of ordinary skill in the art to employ such a method.

Moreover, for the reasons discussed above with respect to Hawtof ‘823 patent, the Blackwell ‘656 patent does not teach or suggest a combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock, nor does it teach or suggest that the liquid feedstock can be atomized by injection into the stream of combustion gas. While the Blackwell ‘656 patent teaches optional atomization by a conventional atomizer apparatus, e.g., a pneumatic atomizer or airblast atomizer (see col. 8, lines 26-54; col. 9, lines 30-55), or a high-velocity flowing “carrier gas” stream, e.g., oxygen, followed by introduction of the atomized liquid feedstock into a burner unit, i.e., a flame (see, e.g. col. 8, lines 46-54), the Blackwell ‘656 patent does not teach that the liquid feedstock can be *atomized by injection* into the combustion gas, nor does it teach that the liquid feedstock can be *atomized by the force of the combustion gas stream* (see para. 0024 of the specification). Accordingly, the combination of the Rohr ‘560 patent and the Blackwell ‘656 patent fails to teach or suggest all of the limitations of the pending claims and, therefore, does not render the claimed invention obvious.

Finally, the combination of the Rohr ‘560 patent and the Pearson ‘076 patent similarly fails to render the claimed invention obvious. First, the Pearson ‘076 patent is directed to an improved burner nozzle and process for making synthetic or fuel gas, via the partial oxidation of a slurry containing solid carbonaceous fuel (see, e.g., col. 1, lines 11-19). Nowhere does the Pearson ‘076 patent mention metal oxide particles, let alone a process for producing fumed metal oxide particles. A person of ordinary skill in the art of the claimed invention, i.e., fumed metal oxides particles and methods of making the same, would not look to art related to the production of synthetic gas or fuel gas. Accordingly, the Pearson ‘076 patent is not pertinent art to that of the claimed invention and cannot properly form the basis of an obviousness rejection.

In any event, the Pearson ‘076 patent fails to cure to deficiencies of the Rohr ‘560 patent. The Office Action alleges that the Pearson ‘076 patent teaches “a burner nozzle ... comprising an admixture to be reacted at a sonic velocity for the purpose of atomizing the admixture” (Office Action, p. 3). However, the Pearson ‘076 patent does not teach or suggest a combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock (see element (b) of pending claim 1). Specifically, the Pearson ‘076 patent discloses atomizing the admixture “before it enters the reactor” (col. 2, lines 43-44), and then

“reacting the admixture in the reactor to form the partially oxidized gas mixture containing hydrogen and carbon monoxide” (col. 2, lines 45-47; see also col. 6, lines 17-29). The admixture is optionally further atomized, still before entering the reactor, by being passed through an exit orifice at an accelerated velocity (col. 6, lines 27-29). Accordingly, the Pearson ‘076 patent discloses atomization of the admixture, *followed by* entry of the admixture into a reactor, but does not disclose a stream of combustion gas having a linear velocity that atomizes and combusts or pyrolyzes the liquid feedstock, as is required by the pending method claims. Accordingly, the combination of the Rohr ‘560 patent and the Pearson ‘076 patent fails to teach or suggest all the limitations of the pending claims and, therefore, does not render the claimed invention obvious.

Because the Rohr ‘560 patent, in combination with any one of the Hawtow ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent, fails to teach or suggest all of the limitations of pending claims 1-3, 7-10, 13-14, 17-18, and 20, the invention defined by these claims cannot properly be considered obvious over these references. Accordingly, the rejection under Section 103 should be withdrawn.

The Office Action also alleges that, because the Rohr ‘560 patent teaches the claimed process, the Rohr ‘560 patent inherently discloses the product that results from the process as defined by pending claims 25-30. Thus, the Office Action’s rejection of claims 25-30 based on the Rohr ‘560 patent is predicated on the assumption that the Rohr ‘560 patent discloses the claimed process. As discussed above, this assumption is incorrect. Furthermore, the combination of the Rohr ‘560 patent with any one of the Hawtow ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent similarly fails to render the claimed process obvious. Accordingly, it cannot be presumed that the Rohr ‘560 patent, either alone or in combination with any of the Hawtow ‘823 patent, the Blackwell ‘656 patent, or the Pearson ‘076 patent, inherently discloses or renders obvious the product of pending claims 25-30. As such, the rejection under Section 103 should be withdrawn.

## 2. *The Rohr ‘560 Patent and the Lewis ‘090 Patent*

The Office Action rejects claims 11 and 12 as allegedly obvious over the Rohr ‘560 patent in combination with the Lewis ‘090 patent and any one of the Hawtow ‘823 patent, the Blackwell ‘656 patent, and the Pearson ‘076 patent.

Claims 11 and 12 are dependent on, and therefore include all of the limitations of, claim 1, which is discussed above in connection with the Rohr '560 patent. As noted above, the Rohr '560 patent, in combination with any of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent, fails to render the claimed invention obvious. The Lewis '090 patent fails to satisfy the deficiencies of these references.

The Lewis '090 patent discloses atomization of a mixture of the liquid feedstock and hexane (col. 4, line 64 – col. 5, line 9), *followed by* introduction of a combustion gas (col. 5, lines 13-17), but does not disclose atomization by injection into the stream of combustion gas as required by the pending claims. Accordingly, the combination of the Lewis '090 patent with the Rohr '560 patent, and any one of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent, fails to teach or suggest all of the limitations of claims 11 and 12, and, therefore, does not render the subject matter of these claims obvious. The rejection under Section 103, therefore, should be withdrawn.

### 3. *The Hung '566 Patent*

The Office Action alleges that claims 1-6 and 13-24 are obvious over the Hung '566 patent in combination with any one of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent. The Office Action further alleges that claims 11 and 12 are obvious over the Hung '566 patent in combination with the Lewis '090 patent and any one of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent.

The Hung '566 patent may not be used to show that the claimed subject matter is obvious. The Hung '566 patent qualifies as prior art only under 35 U.S.C. § 102(e), and the Hung '566 patent and the claimed invention were, at the time the claimed invention was made, owned by the same person or subject to an obligation of assignment to the same person, namely Cabot Corporation, as evidenced by the recorded assignments for the Hung '566 patent and the present application. As a result, the Hung '566 patent cannot be utilized as prior art under 35 U.S.C. § 103 against the claimed invention.

Without the Hung '566 patent, which, for the reasons discussed immediately above, cannot properly support an obviousness rejection of the pending claims, only the combination of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent is left to support the rejection of claims 1-6 and 13-24. For the reasons discussed above with respect

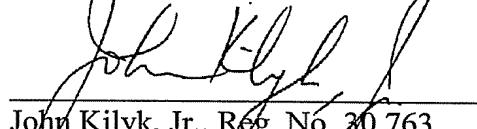
to the Rohr '560 patent, each of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent, even if considered as a group in combination with the Rohr '560 patent, fails to teach or suggest all of the limitations of the pending claims. As such, the combination of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent fails to teach or suggest all of the limitations of claims 1-6 and 13-24 and, therefore, does not render the invention defined by these claims obvious. Accordingly, the obviousness rejection of claims 1-6 and 13-24 should be withdrawn.

Similarly, without the Hung '566 patent, only the Lewis '090 patent, in combination with any one of the Hawtof '823 patent, the Blackwell '656 patent, and the Pearson '076 patent, is left to support the rejection of claims 11 and 12. For the reasons discussed above with respect to the Lewis '090 patent, this combination fails to teach or suggest all of the limitations of the pending claims, and, therefore, does not render claim 11 or 12 obvious. Accordingly, the obviousness rejection of claims 11 and 12 should be withdrawn.

*Conclusion*

Applicants respectfully submit that the patent application is in condition for allowance. If, in the opinion of the Examiner, a telephone conference would expedite the prosecution of the subject application, the Examiner is invited to call the undersigned attorney.

Respectfully submitted,



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## SILICA, AMORPHOUS

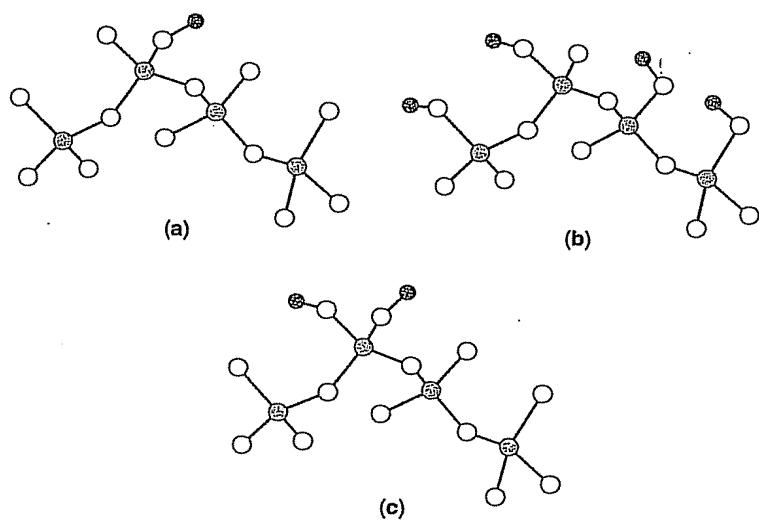
### 1. Introduction

Amorphous silica, ie, silicon dioxide [7631-86-9],  $\text{SiO}_2$ , does not have a crystalline structure as defined by X-ray diffraction measurements. Amorphous silica, which can be naturally occurring or synthetic, can be either surface-hydrated or anhydrous. Synthetic amorphous silica can be broadly divided into two categories of stable materials (1): vitreous silica or glass (qv), which is made by fusing quartz at temperatures greater than  $\sim 1700^\circ\text{C}$  (see SILICA, VITREOUS SILICA), and microamorphous silica, which is discussed herein.

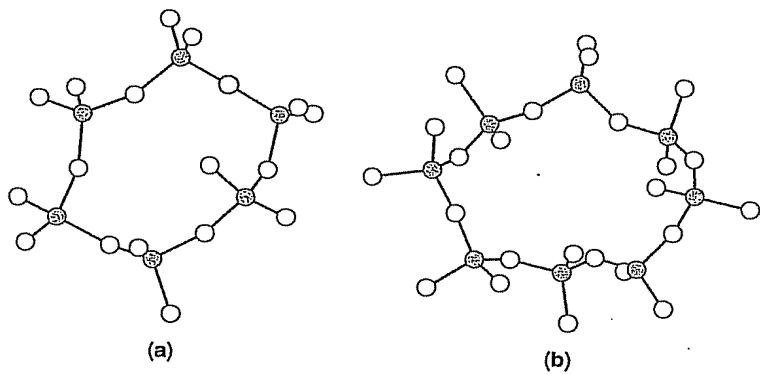
Microamorphous silica includes silica sols, gels, powders, and porous glasses. These consist of ultimate particles of the inorganic polymer  $(\text{SiO}_2)_n$ , where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane,  $-\text{Si}-\text{O}-\text{Si}-$ , or a silanol,  $-\text{Si}-\text{O}-\text{H}$ , functionality. The bond distances and bond angles in amorphous silica are similar to those of cristobalite [14464-46-1] (2):  $\text{Si}-\text{O}$  bond distances are  $\sim 0.16$  nm, and  $\text{Si}-\text{O}-\text{Si}$  bond angles are  $\sim 148^\circ$ . Surface silanol groups can be isolated from one another, so that intramolecular hydrogen bonding does not occur (Fig. 1a); vicinal to one another, thus promoting the formation of intramolecular hydrogen bonding (Fig. 1b); or geminal to one another, whereby two silanol groups are bonded to the same silicon atom (Fig. 1c). Initially formed low molecular weight species condense to form ring structures so as to maximize siloxane and minimize silanol bonds (Fig. 2).

A random arrangement of rings leads to the formation of complex structures of generally spherical particles less than  $\sim 100$  nm in diameter (3) (Fig. 3). These particles have high surface area values, generally greater than  $\sim 3 \text{ m}^2/\text{g}$ . Crystallinity is usually determined spectroscopically by using X-ray diffraction (4) to establish the absence or presence of definitive lines in the diffraction pattern of silicas. For example, Fig. 4 shows X-ray diffraction patterns of crystalline quartz sand (Fig. 4a) and of cristobalite (Fig. 4b). Both exhibit distinct reflections that can be used for identification. The X-ray diffraction patterns of four commercial synthetic amorphous silicas are shown in Fig. 5. The colloidal silica (Fig. 5a) is a sol or stable dispersion of discrete particles. There is a general absence of definitive reflections in these curves. Studies of radial distribution function curves of a vitreous silica have indicated that regions of local atomic order can exist that approximate the cristobalite structure. Whereas amorphous silica is closely related to the cristobalite structure, this local order is believed to be limited to crystalline domains of up to 2 nm in diameter that have completely random orientations and that are thus statistically distributed (5). Sharp X-ray diffraction patterns (lines) would therefore not be obtained.

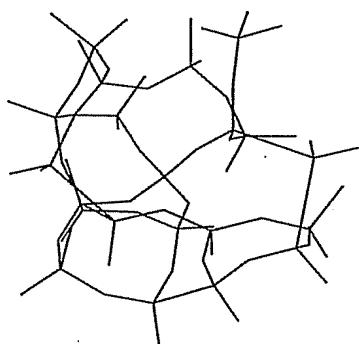
Chemical methods to determine the crystalline content in silica have been reviewed (6). These are based on the solubility of amorphous silica in a variety of solvents, acids, or bases, with respect to relatively inert crystalline silica, and include differences in reactivity in high temperature fusions with strong bases. These methods are qualitative, however, and fail to satisfy



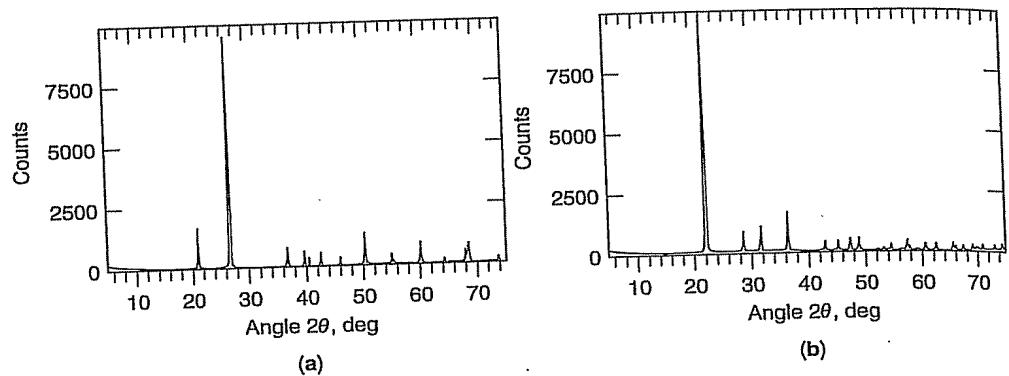
**Fig. 1.** Silanol groups of amorphous silica surface, where  $\oplus = \text{Si}$ ;  $\circ = \text{O}$ ; and  $\oplus = \text{H}$ :  
 (a) isolated, (b) vicinal, and (c) geminal.



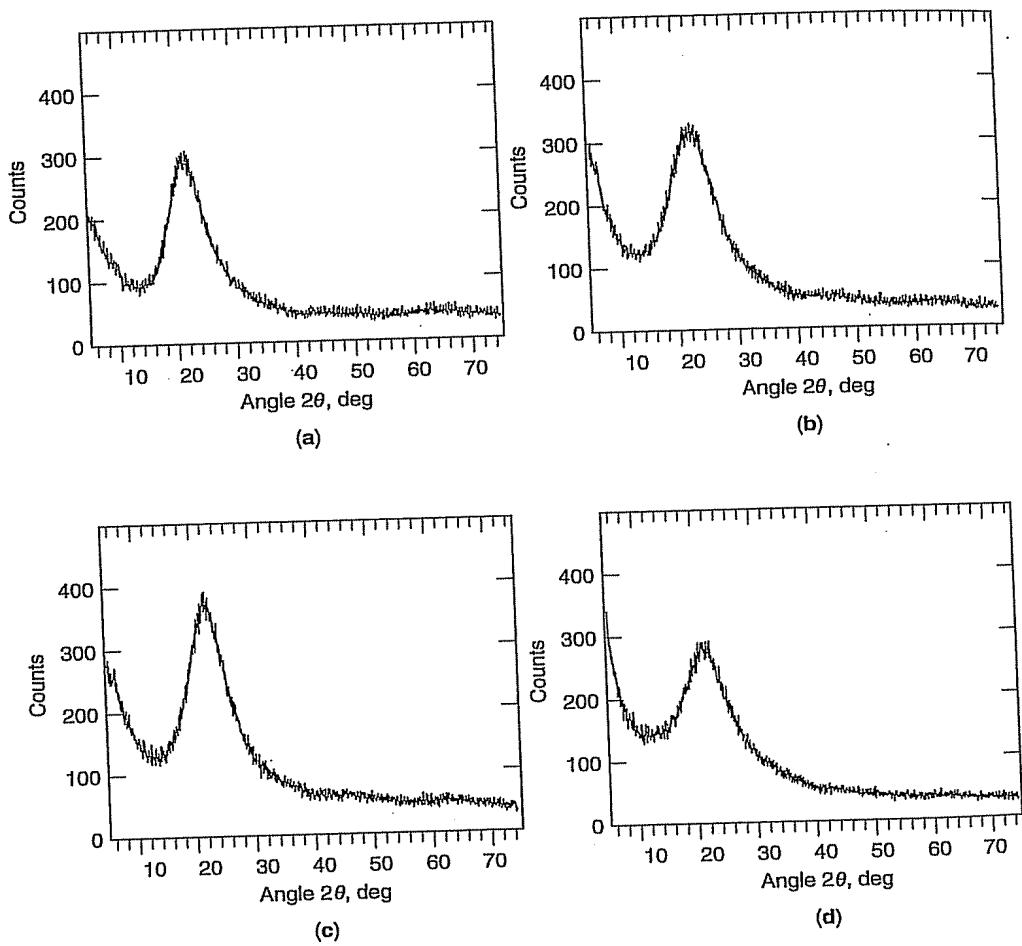
**Fig. 2.** Silica ring structures, where  $\oplus = \text{Si}$ ;  $\circ = \text{O}$ : (a) 12-membered  $\text{SiO}_2$  hexamer, and  
 (b) 16-membered  $\text{SiO}_2$  octamer.



**Fig. 3.** Complex ring structures in  $\text{SiO}_2$  polymer.



**Fig. 4.** X-ray diffraction patterns using a Cu anode: (a) crystalline quartz sand and (b) cristobalite.



**Fig. 5.** X-ray diffraction pattern of commercial samples: (a) colloidal silica, DuPont Ludox TM50; (b) silica gel, Sylodent 700; (c) precipitated silica, PPG Hi-Sil 190; and (d) pyrogenic (fumed) silica, Wacker HDK.

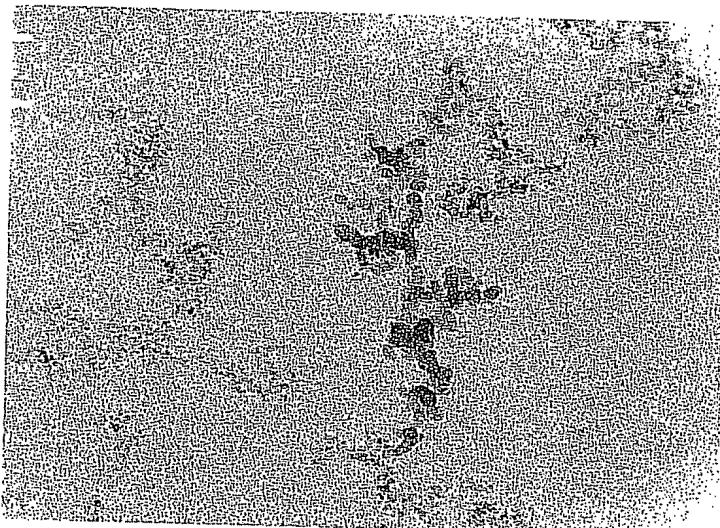


Fig. 6. Transmission electron micrograph of a commercial pyrogenic silica, Wacker HDK. Magnification of 225,000 $\times$ .

regulatory requirements to determine crystallinity at 0.1% concentration in bulk materials.

Microamorphous silica can be divided into microparticulate silica, ie, microscopic sheets and fibers, and highly hydrated silica (1). The microparticulate silicas are the most important group commercially. These include silicas precipitated from aqueous solution and silicas formed in the vapor phase, called pyrogenic or fumed silica. Several synthetic routes exist to prepare any form of microporous silica, where microporous often refers to the ability of the silica to adsorb gases or liquids. For example, pyrogenic silica can be prepared by either (1) vaporizing silicon dioxide in an arc or in a plasma jet, and condensing it in an inert gas; (2) oxidizing the more volatile silicon monoxide, SiO, in the vapor phase with air, and condensing it; or (3) oxidizing silicon compounds (qv), eg, SiH<sub>4</sub>, SiCl<sub>4</sub>, or HSiCl<sub>3</sub>, in the vapor phase in a hydrocarbon flame, and then condensing to produce branched-chain aggregates of silica up to ~1  $\mu\text{m}$  in length (Fig. 6). Pyrogenic silica is collected as a finely divided powder.

Amorphous silica formed in aqueous solution can occur as sols, gels, or particles. A silica sol can either consist of polysilicic acid having a molecular weight of SiO<sub>2</sub> up to ~100,000, or be a stable dispersion of fine colloidal particles of diameters >5 nm (Fig. 7). A silica gel has a three-dimensional, continuous structure (Fig. 8). Macroscopic particles formed by aggregation of a sol or very small particles of a gel to afford bunched aggregates of silica up to approximately 1  $\mu\text{m}$  in diameter are called precipitated silica (Fig. 9). This is collected as a powder by physically agglomerating these aggregates and evaporating the water.

Microscopic sheets of amorphous silica have been prepared in the laboratory by either (1) hydrolysis of gaseous SiCl<sub>4</sub> or SiF<sub>4</sub> to form monosilicic acid

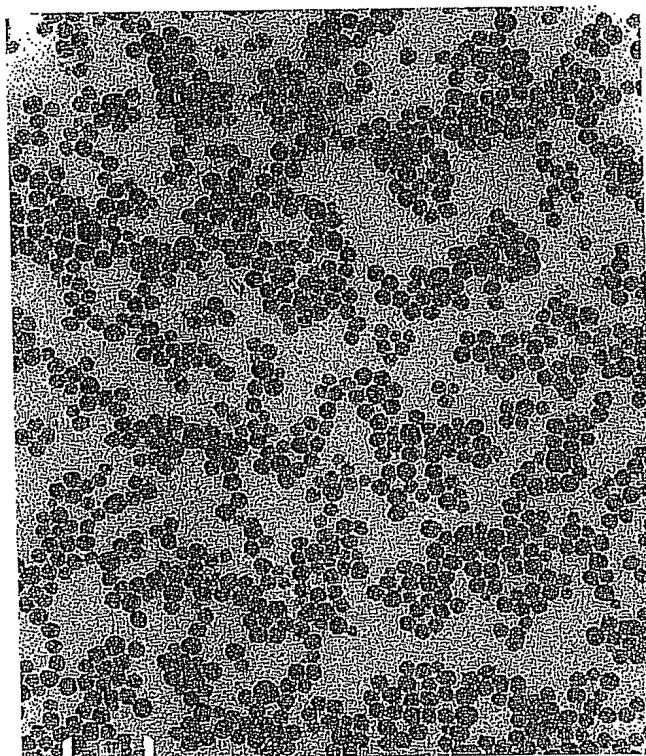


Fig. 7. Transmission electron micrograph of a commercial colloidal silica, DuPont Ludox TM50. Magnification of 225,000 $\times$ .



Fig. 8. Transmission electron micrograph of a commercial silica gel. Magnification of 300,000 $\times$ .

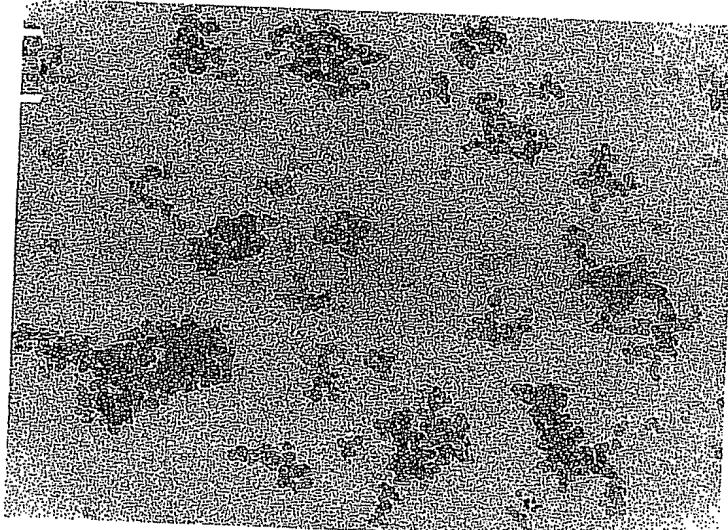


Fig. 9. Transmission electron micrograph of a commercial precipitated silica, PPG Hi-Sil 190. Magnification of 225,000 $\times$ .

[10193-36-9] (orthosilicic acid),  $\text{Si}(\text{OH})_4$ , with simultaneous polymerization in water of the monosilicic acid that is formed (7); (2) freezing of colloidal silica or polysilicic acid (8–10); (3) hydrolysis of  $\text{HSiCl}_3$  in ether, followed by solvent evaporation (11); or (4) coagulation of silica in the presence of cationic surfactants (12). Amorphous silica fibers are prepared by drying thin films of sols or oxidizing silicon monoxide (13). Hydrated amorphous silica differs in solubility from anhydrous or surface-hydrated amorphous silica forms (1) in that the former is generally stable up to 60°C, and water is not lost by evaporation at room temperature. Hydrated silica gel can be prepared by reaction of hydrated sodium silicate crystals and anhydrous acid, followed by polymerization of the monosilicic acid that is formed into a dense state (14). This process can result in a water content of approximately one molecule of  $\text{H}_2\text{O}$  for each silanol group present.

## 2. Characterization

Amorphous silica is distinguished by chemical composition, physical properties, and characteristics of the particles. Exact analytical procedures depend on the type and intended application of the amorphous silica. The most important chemical information is the amount of silica, %  $\text{SiO}_2$ ; percentage of associated water, determined by weight loss at 105°C; total solids content of nonoxidizable materials, determined by weight loss upon ignition at ~1200°C; presence of stabilizers, eg, formaldehyde (1); carbon content, such as carbon dioxide, carbonate, and organic carbon, determined by combustion to carbon dioxide; level of soluble salts, eg, chloride and sulfate, determined by X-ray fluorescence

Table 1. Test Methods for Characterizing Amorphous Silica

Property tested	Test methods
color	ISO 787, Parts I, XII; ISO 5794, Part I
average particle size	ASTM C721, D1366, E20, E523, and F660; ISO 787, Part XVIII
SiO <sub>2</sub> content	ASTM C575 and D297; ISO 5794, Part I
coarse, insoluble material	ASTM C117 and D185; ISO 787, Parts III, VI, VII, and VIII; ISO 5794, Part I
volatile matter (water)	ISO 787, Part II
specific surface area	ASTM D1993 and D5604; ISO 5794, Part I; NF T 45-007
bulk density	ASTM D604; ISO 787, Parts X, XI
mean projected area of aggregates	ASTM D3894
metal ion and salt content	ASTM C575 and D719; ISO 5794, Part I, Annexes A, B, C, D
absorption of oil	ASTM D2414; ISO 787, Part V
pH	ASTM D1512; ISO 787, Parts IV, IX
porosimetry	ASTM D4284
occupational exposure	ASTM E1156

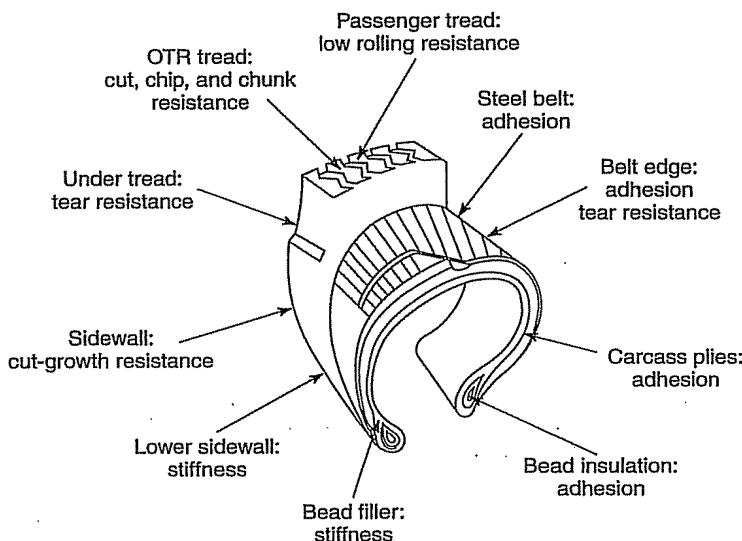
spectroscopy (15) or by chemical methods, eg, extraction; level of nonsiliceous ash; level of metal impurities, determined by X-ray fluorescence, eg, aluminum, sodium, calcium, manganese, and iron, or by atomic absorption, eg, copper and chromium; and silanol group density, determined by infrared (ir) spectroscopy (16) or chemical titration.

Physical characteristics include measurements of pH determined as a 5% aqueous slurry, density and tamped density, viscosity, turbidity, refractive index, light-scattering properties, and/or sedimentation rate by ultracentrifugation. Silica particles are characterized by specific surface area as determined by the adsorption of nitrogen gas by the BET method (17) or by the adsorption of cetyltrimethylammonium bromide (CTAB) (18); average particle size and size distribution; sieve residue; porosity such as average pore diameter and pore volume as determined by intrusion of mercury or adsorption of nitrogen gas (19); degree of aggregation as determined by mean projected area (MPA) measured using transmission electron microscopy (20); oil absorption, eg, dibutylphthalate, dioctylphthalate, or linseed oil; and rate of dissolution. Particle size is measured by transmission electron microscopy (21), light scattering, absorbance of visible light, low angle X-ray scattering, centrifugation, rate of reaction with molybdic acid, or surface area measurement of dried particles. Table 1 is a summary of standard test methods used to characterize amorphous silica follows:

The typical range of properties for commercial colloidal silicas, silica gels, precipitated silicas, and pyrogenic silicas is given in Table 2.

### 3. Commercial Production

In 2004, ~36% of synthetic amorphous silica production capacity is in Europe, followed by North America at 26%, China at 25% (estimated), and



**Fig. 14.** Schematic of a passenger tire showing individual components and use of precipitated silica to improve rubber compound performance. OTR = off-the-road.

## 8. Pyrogenic Silica

**8.1. Properties.** Amorphous pyrogenic (fumed) silicas are fluffy white powders that are generally less dense and of higher purity than are silicas precipitated from solution. Pyrogenic silicas have a much lower hydrated surface and are sometimes completely anhydrous. Surface silanol density normally ranges from  $2\text{--}4/\text{nm}^2$  of surface area. The particle size is controlled by combustion conditions during the flame hydrolysis. Pyrogenic silicas having surface areas  $<300\text{ m}^2/\text{g}$  are essentially nonporous, whereas those having higher surface areas can have some porosity. They generally can contain a few hundred ultimate particles fused into branched-chain, 3D aggregates (56) (eg, see Fig. 6). Pyrogenic silicas in the 100-nm to 2- $\mu\text{m}$  diameter particle size range are common (86).

**8.2. Preparation.** Pyrogenic silica can be prepared in several ways, including vaporizing silica and oxidizing organic or inorganic silicon compounds. Vaporizing silica at high temperatures of  $\sim 2000^\circ\text{C}$  forms anhydrous amorphous silica particles upon cooling. In the presence of a reducing agent, eg, coke, silica sublimes at  $\sim 1500^\circ\text{C}$  to produce the volatile silicon monoxide,  $\text{SiO}$ , which can then be oxidized to produce particulate fumed silica,  $\text{SiO}_2$ . Oxidation of silicon tetrachloride,  $\text{SiCl}_4$ , vapor at high temperatures produces fumed silica and  $\text{Cl}_2$ . Alternatively, silicon tetrachloride can be burned in the presence of methane,  $\text{CH}_4$ , or hydrogen,  $\text{H}_2$ , gases to produce fumed silica,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ . The latter process is an important commercial method (Fig. 15) (56). Silicon ester vapors can be oxidized and hydrolyzed to produce particulate silica of high purity, though at high cost. Silicon tetrafluoride,  $\text{SiF}_4$ , a by-product of the phosphate fertilizer industry, can also be used to produce pyrogenic silica by hydrolysis of the vapor at  $1600\text{--}2200^\circ\text{C}$ . HF is a by-product that can then react with sand to produce more  $\text{SiF}_4$  (1,87).

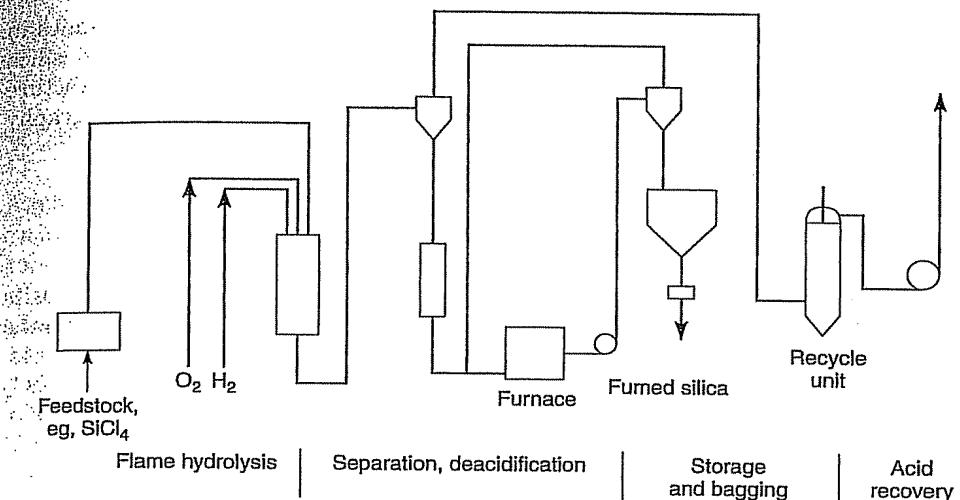


Fig. 15. Schematic of pyrogenic silica production (56). See Fig. 13 for definitions.

**8.3. Applications.** Pyrogenic or fumed silica production in 2002 was estimated to be 120,000 metric tons (38). Cabot and Degussa in the United States and in Europe, General Electric (United States), Wacker-Chemie (Germany), Nippon Aerosil (Japan), and Tokuyama Soda (Japan) were the largest manufacturers. Pyrogenic silica is used in rubber applications that require a low level of surface water per unit surface area of the silica, primarily as a reinforcement in adhesives, sealants (88), and elastomer compounds based on silicone polymers (89,90). Pyrogenic silica also has a variety of other uses. It serves as a thixotropic agent in plastics, eg, in polyester casting resins; gel coats (91); sealants and adhesives (92); cosmetics in ointments and lotions (93); toothpastes; coatings (91); printing inks (94); free flow, antistatic agent in animal feedstuffs and hygroscopic powders; carrier for active ingredients, eg, pharmaceuticals (qv), catalysts, and liquid spice extracts (95); gloss control agent in coatings and foils (56); coating additive to improve the mechanical reliability of fused silica optical fibers (96); and antifoaming or defoaming agent in the manufacture of paper, decaffeinated coffee and tea, poultry and seafood processing, and oil refining (97).

## 9. Fused Silica

Transparent fused silica can be formed at a temperature of  $1200^\circ\text{C}$  and a pressure of 13.8 MPa (2000 psi) from silica powder consisting of 15-nm ultimate particles (98) or by electric arc fusion of pure silica sand having low iron and alkali metal contents. The cooled product is ground to the desired particle size, usually powders  $>8 \mu\text{m}$  in diameter. Fused silica is primarily manufactured by C-E Minerals, MINCO, and Precision Electro Minerals in the United States; by Didier-Werke (Germany), Frank and Schulte (Germany), Saint-Gobain Quartz (United Kingdom), Sico (Austria), and Vesuvius (France) in Europe; by Denki Kagaku

Kogyo, Kinsei Matec, Micron, Tatsumori, Tokuyama, and Toshiba Ceramics Japan. Based on 2002 data, an estimated 170,000 metric tons of fused silica were used as a sacrificial component or investment casting in the manufacture of metals and as a component in refractory materials (99) and in the lithograph industry (100).

## 10. Naturally Occurring Amorphous Silica

**10.1. Formation.** Most naturally occurring amorphous silica deposits are biogenic forms deposited from the exoskeleton, plates, or spines of aquatic organisms, eg, diatoms, radiolarians, silicoflagellates, and certain sponges. These organisms extract silica from very dilute solutions, eg, 0.1 ppm of SiO<sub>2</sub> or 2 mmol/kg, and are found in both marine and freshwater environments. Large deposits of these materials are found as loosely coherent chalk-like sediments in the equatorial Pacific area, ie, radiolarians, and in high latitude areas of all oceans, ie, diatoms. All biogenic silicas are noncrystalline because the kinetic barrier to crystallization is high [ $\sim 800 \text{ kJ/mol}$  (191 kcal/mol)] in neutral aqueous environments. In all these structures, the mineral exists as hydrated, covalent inorganic polymer having the general structure  $(\text{SiO}_4)_n(\text{OH})_{4-n}m$ , where  $m$  is a large integer representing the degree of polymerization and  $n$  ranges from 0 to 4 to indicate the degree of hydration (101).

The silica structure has a close relationship to the cellular structure of the organism. Silica is deposited as gels, sheets, fibers, tubes, and globular assemblies. It has been found that the macroscopic geometric structure of the deposited silica is replicated in the short-order (two–three siloxane unit) structure (101). Although the dissolution of silica is inhibited by inclusion of various metal ions in the structure and often an organic coating, these deposits are converted over millions of years to opal-CT and opal-C, which are well-crystallized cristobalite (102). These siliceous materials are also transformed by dissolution, precipitation, recrystallization, and compaction over geological time to form a less soluble denser material, which is called chert if granular, chalcedony if fibrous, or flint, dark gray. Amorphous silica can be formed by the alteration of sand to a colloidal ally subdivided high surface area, amorphous silica volcanic ash (1). Amorphous silica is sometimes precipitated from the hot supersaturated waters of hot springs (siliceous sinter) and geysers (geyserite) where it is often found along with calcareous sinter (103,104).

**10.2. Applications.** The most significant commercial material from the biogenic silicas is diatomaceous earth [7631-86-9], also called kieselguhr or diatomite (qv). These deposits are the sediment of fragments and shells of one-celled algae, which form very fine particles having high surface area and as high as 94% silica content. Initially, silica in diatomite is amorphous, but portions of these deposits have been converted to cryptocrystalline quartz (103). Approximately 1,500,000 metric tons of diatomaceous earth were used in 1994 as absorbents, fillers, insulating materials, and polishing agents, primarily in China, France, Germany, Italy, Korea, Mexico, and the United States. Tripoli, a white-to-gray, soft, porous material used as an abrasive or a filler, is mined from the Devonian deposits in southern Illinois. It is sold as amorphous silica.

## SILICA, VITREOUS

### 1. Introduction

Vitreous silica [60676-86-0] is an amorphous phase of silicon dioxide. Modern methods of manufacture use chemical precursors to prepare the glass, however, vitreous silica was traditionally formed by heating crystalline  $\text{SiO}_2$  above its melting point,  $1730 \pm 5^\circ\text{C}$  (1), and then cooling it rapidly enough to avoid recrystallization. Because molten  $\text{SiO}_2$  is extremely viscous, glass formation is possible at a relatively slow cooling rate. Vitreous silica is available in a variety of forms, including powders, coatings, fibers, porous bodies, and bulk (dense) glass. This article focuses, for the most part, on the processing, properties, and uses of the bulk glass (see SILICA, AMORPHOUS SILICA).

Vitreous silica has a wide range of commercial and scientific applications. Its unique combination of physical properties includes good chemical resistance, minimal thermal expansion, high refractoriness, and excellent optical transmission from the deep ultraviolet (uv) to the near-infrared (ir).

Although vitreous silica is a simple, single-component glass, its properties can vary significantly, depending on thermal history, the type and concentration of defects, and the presence of dopants and impurities. Vitreous silica can, however, be one of the purest commercially available glassy materials. In synthetic vitreous silicas, eg, total metal contamination is typically measured in the 50–100 ppb range. Even at such a low level of impurities, differences in properties, eg, uv transmission, are observed for various silicas.

Vitreous silica is a difficult material to manufacture, and as such is more expensive than most commercial glasses. It has a high vapor pressure, a strong tendency to devitrify, and a high viscosity even at its melting point. These physical characteristics preclude the use of standard glass-forming techniques. For optical-quality glass in particular, there is a need to maintain high purity and obtain excellent homogeneity of the refractive index; these specifications have, in part, led to the development of several unique manufacturing approaches, eg, electric fusion and flame hydrolysis.

Vitreous silica is known largely as a synthetic material, but there are instances of the material occurring in nature (2,3). Vitreous tubes called fulgurites are produced when lightning fuses quartz sand. Large deposits of fulgurite exist in the Libyan desert. Vitreous silica can also be produced by meteor impact. The impact leads to rapid adiabatic heating of the quartz above its melting point. The quartz forms a glass on cooling. Examples of this type of vitreous silica have been found near Canyon Diablo, Arizona, and in meteorite craters in Australia and Arabia.

Vitreous silica is known by a number of names, most of which were developed to describe vitreous silicas formed using a particular processing method (4–6). These names are often misapplied as generic names for all vitreous silicas. Silica (qv) is a general term that refers to all forms of silicon dioxide, both crystalline and glassy; silica glass is an ambiguous term because it sometimes refers to any silica-containing glass composition; fused silica applies to vitreous silicas formed by fusion; fused quartz refers to vitreous silica formed specifically by the direct melting of quartz crystals; and synthetic fused silica describes

Table 1. Classification of Commercial Vitreous Silicas

Type	Method	Impurities, ppm			Representative glasses
		OH	Cl	Cations	
I	electric melting of quartz	<20	0	50–300	Infrasil, Vitreosil-ir, GE-124, GE-214
II	flame fusion of quartz	200–500	0	10–50	Homosil, Optosil, Vitreosil-O55
III	flame hydrolysis	600–1200	50–100	<1	Corning 7980, Dynasil 1000, Shinetsu P-10, Spectrosil, Suprasil, NSG-ES
IV	oxidation of $\text{SiCl}_4$ (plasma)	<20	<200	1–2	Spectrosil WF, Suprasil-W
V	sol-gel	<1	<1–500	<1	GELSIL

vitreous silicas formed from chemical precursors, such as silicon tetrachloride. Uses of the terms quartz and quartz glass should normally be avoided. These confuse vitreous silica with quartz, a crystalline form of silicon dioxide.

The optical quality of vitreous silica can range from transparent to opaque. Opaque glass contains a large number of isolated bubbles ranging in size from 5 to 200  $\mu\text{m}$  (7). The bubbles scatter light, giving the glass a milky appearance. This material, produced by melting quartz sand, also tends to be less pure (99.5–99.9 wt%  $\text{SiO}_2$ ) than more transparent materials. The opaque glass is an inexpensive form of vitreous silica and is often used where purity and optical properties are not important.

Transparent vitreous silicas have historically been classified by an informal scheme that differentiates the glasses by manufacturing method (8–10). Five general types of commercial glasses are listed in Table 1. Although this list gives a good overview of the available glasses, it is not complete. Many of the listed manufacturing methods have processing variations that can alter glass chemistry and properties. Moreover, the Type V designation is not as widely recognized as the others. Also, the list does not include the hybrid processes that combine some of the key features of different methods. For example, there have been efforts to produce glass by flame-fusing sol-gel produced powder (11).

## 2. Structure

Vitreous silica is considered the model glass-forming material, and as a result has been the subject of a large number of X-ray, neutron, and electron diffraction studies (12–16). These investigations provide a detailed picture of the short-range structure in vitreous silica, but questions about the long-range structure remain.

The basic structural element in both vitreous and crystalline silica is the  $\text{SiO}_4^{4-}$  tetrahedron, which arises from the  $sp^3$  hybrid orbitals of the silicon. Each silicon atom sits in the center of the tetrahedron surrounded by four oxygen atoms that hold the corner positions. Tetrahedrons bond together by corner sharing. In a properly developed structure, each oxygen is shared by only

two tetrahedrons. This bonding scheme can produce a large variety of three-dimensional (3D) structures and is the reason that silica has a number of crystalline phases.

The bonding scheme can also accommodate a large degree of disorder without breaking the Si-O links. Diffraction studies on vitreous silica show that the randomness of the structure results from variations in the Si-O-Si bond angle. The individual  $\text{SiO}_4^{4-}$  units do not show significant distortion. The O-Si-O bond angle is fixed at 109.5°, expected in a symmetric tetrahedral configuration, and the Si-O bond distance, 161 pm, is the same as that observed in the crystalline silica phases. The Si-O-Si bond angles, on the other hand, show a distribution that varies from 120 to 180°. Whereas original analysis of the X-ray measurements placed the maximum of the angle distribution at ~144°, a more recent reexamination of the data showed the most probable bond angle to be 152° (17). High temperature X-ray measurements show that the bond distances are constant up to 1000°C (18).

In the crystalline form of silica, the  $\text{SiO}_4^{4-}$  tetrahedrons link together in a series of interconnecting, six-membered rings. In the glassy form, the tetrahedral network can be modeled using a distribution of ring sizes normally ranging from three- to eight-membered units (19). The six-membered ring is the most common size but it can exist in distorted configurations which are not present in the crystalline structures. Detailed ring statistics of the glassy phase cannot be extracted directly from diffraction data. The three- and four-membered rings have been studied using Raman scattering (20,21).

The longer range structure of vitreous silica has been the subject of much debate. Two basic models have been presented (14,22,23). The random network model assumes that the  $\text{SiO}_4^{4-}$  tetrahedrons are connected in a completely random fashion and that there are no ordered microregions. The crystallite-based models argue that vitreous silica consists of very small, randomly oriented microcrystals. These regions are assumed to be 0.7–2.0 nm in size and connected by noncrystalline boundary regions. One problem of the crystallite models is that, because of the small sizes proposed for the crystallites, the fraction of atoms in the boundary regions should be significant and include species, e.g.,  $\text{O}_\text{s}=\text{Si}$  double bond, where  $\text{O}_\text{s}$  signifies an oxygen on the surface of the crystallite. There are, however, no indications of large concentrations of these species in the diffraction and vibrational spectra in as-formed vitreous silica (24,25). As a counterpoint, several researchers have suggested that the anomalous changes seen in a number of the physical properties of vitreous silica near the transformation temperatures of the crystalline phases occur because the atomic arrangements present in vitreous silica relate, to some extent, to crystalline structures (26).

The tetrahedral network can be considered the idealized structure of vitreous silica. Disorder is present, but the basic bonding scheme is still intact. An additional level of disorder occurs because the atomic arrangement can deviate from the fully bonded, stoichiometric form through the introduction of intrinsic (structural) defects, dopants, and impurities. These perturbations in the structure have significant effects on many of the physical properties. A key concern is whether any of these entities breaks the Si-O bonds that hold the tetrahedral network together. Fracturing these links produces a less viscous structure that can respond more readily to thermal and mechanical changes.

The intrinsic defects include paramagnetic and diamagnetic species (24,27,28). The paramagnetic defects have received the most study because they are readily detectable by electron spin resonance (esr) spectrometry. Paramagnetic defects that have been identified by esr include the E' center, the non-bridging oxygen hole center; and the peroxy radical. All of these defects are normally induced in vitreous silica by ionizing radiation or uv light.

A number of diamagnetic defects are also believed to exist in vitreous silica. Because there is no direct way to study these species, their identification is either done indirectly, eg, by uv absorption, or by employing esr after the material has been made paramagnetic using ionizing or laser irradiation. The proposed diamagnetic species include the neutral oxygen vacancy, the doubly coordinated silicon, and the peroxy bond. The diamagnetic defects occur when the glass-forming conditions are off-stoichiometry.

The impurity (extrinsic) defects include nonmetallic and metallic additives or contaminants (29-32). The nonmetallic contaminants are the more prevalent type in most high grade vitreous silicas. In the synthetic silicas, eg, the concentrations of nonmetals can be three to five orders of magnitude higher than that of metals. The nonmetallic contaminants include species, eg, hydrogen, chlorine, fluorine, and oxygen, which can be present in the furnace atmosphere during certain forming, consolidation, or special annealing treatments. These impurities exist in the vitreous silica in a variety of forms. They can link directly to the silica network, eg, hydroxyl, Si-OH bonding; hydride, Si-H, bonding; and chloride, Si-Cl, bonding; or exist interstitially as molecular species, such as H<sub>2</sub>, H<sub>2</sub>O, Cl<sub>2</sub>, and O<sub>2</sub>. Metallic contaminants are usually picked up from the silica raw material or from the furnace materials during processing. These dissolve in the silica network by bonding in some way to the oxygen ions. Table 2 lists the metal impurities commonly seen in vitreous silicas.

### 3. Manufacturing

Vitreous silica, a hard glass having a limited working range, is not conveniently produced using conventional glass-melting techniques. Rather, its high melting point and high melt viscosity have forced the development of a number of unique forming methods that utilize sintering or some type of deposition process. Many of the key physical properties depend on the specific forming process used because the forming process defines the material's thermal history and impurity-dopant profile. However, in most cases these developments have led to very high purity glasses with high index homogeneity and other properties that can be largely engineered.

**3.1. History.** The first reported instances of fusing silicon dioxide occurred early in the nineteenth century. In 1813, fusing of small crystals of quartz by injecting oxygen into an alcohol flame was described. This was followed in 1821 by the description of the fusing of quartz crystals using a hydrogen-oxygen torch (33). Properties of vitreous silica were first measured in 1839 (34). A glass produced using a hydrogen-oxygen flame exhibited remarkable strength, good elasticity, and excellent thermal shock resistance. This glass

Table 2. Impurity Concentrations in Vitreous Silicas<sup>a</sup>

Impurity, ppm	Translucent vitreous silica	Transparent vitreous silica <sup>b</sup>		
		Type I	Type II	Type III <sup>c</sup>
aluminum	18–176	16	10–50	<0.05
antimony	<0.06	0.3	0.15	<0.005
arsenic	<0.01	<0.4	0.08	<0.005
boron	<0.1	<0.1	0.1	0–0.01
calcium	2.0	0.6	0.8–3.0	<0.1
chromium	<0.09	<0.01	1–2.0	<0.03
cobalt		0.05		0.01
copper	<0.15	<0.1	0.7	0.004
gallium			0–0.008	<0.02
gold	<0.03		0.0003	
hydroxyl	<200	<5	~180	<1250
iron	1	0.3	0.8	<0.12
lithium	1.3	1.0	0–2.0	<0.001
magnesium	0.1	0.1	0.2	<0.05
manganese	0.1	0.1	0.01	<0.01
mercury				<0.01
phosphorus	0.1–1.5	1.5	0.1	<0.001
potassium	1.0	0.7	0.8	<0.1
sodium	2.0–3.0	1.0	1.0	<0.1
titanium	1.1–63	1.1	0.8	<0.04
uranium	<0.04		0.0003	<0.001
zinc				<0.03
zirconium	1.0–1.5	1.5	0–0.1	<0.03

<sup>a</sup>Data taken from manufacturers' publications.<sup>b</sup>See Table 1 classifications.<sup>c</sup>The metallic impurities of Type IV vitreous silica are similar to those of Type III material, except for a negligible hydroxyl content.

also had a tendency to volatilize and to devitrify. Later, the glass was shaped into tubes and bulbs. In 1887, a flame was used to draw fibers of vitreous silica (35).

Several efforts to develop commercial processes began ~1900 and were centered mainly in England, France, and Germany (35). It was during this early commercialization of vitreous silica that the distinction between the opaque and transparent glasses arose. The opaque material, called fused silica, was made by fusing sand. Resistance heating with carbon electrodes was an effective method for generating the desired temperature. The transparent material, called fused quartz, was made by fusing clear, selected quartz crystals. Achieving transparency by this approach required overcoming the problem of bubble formation in the glass. Crystalline quartz undergoes a transformation, ie, an inversion from its low to high crystalline form, at 575°C, which also includes a rapid volume change. If heating is not uniform, the crystals can fracture (splinter) and lead to air encapsulation and the formation of bubble lines. This problem was overcome in 1900 by using the fracturing phenomenon to produce a fine crystalline frit that could be subsequently flame fused without splintering (36,37). Fracturing was promoted by heating the quartz crystals to a red heat and

then quenching in water. An approach in which a glass boule was produced by injecting this powder into a flame was also advanced (38).

The production of vitreous silica from chemical precursors was first described in patents filed in 1934, including a fabrication method in which fine, high purity powders were produced by decomposing silanes (39). Forms were then cast from aqueous slips. More importantly, a flame hydrolysis process which used  $\text{SiCl}_4$  as the chemical precursor was described (40). This latter approach led to a marked improvement in glass purity and served as the basis for the processes used in the 1990s to make synthetic vitreous silica.

**3.2. Modern Manufacturing Techniques.** Modern manufacturing processes of vitreous typically involve the fusion or viscous sintering of silica particles; the particles can be derived from sand crystals or are produced through a chemical process, eg, flame hydrolysis or sol-gel. In one practice of the flame hydrolysis process, the powder is produced and fused into glass a single step, without the isolation of a porous body. Dopant and additive profiles are concentration are then controlled by the deposition conditions. When a process involving a discrete porous silica body as an intermediate is used, subsequent processing steps can be used to control dopant levels and in particular, the hydroxyl level of the final glass. The choice of fabrication method is often dictated by the end-use specifications. Flame hydrolysis or similar chemical techniques that allow for the production of very high purity glass are the methods of choice for optical applications but may be economically wasteful for less demanding applications.

**Translucent Vitreous Silica.** Translucent vitreous silica is produced by fusion of high purity quartz sand crystals (41,42). Sand is packed around a graphite rod through which a current is passed. The resistance heating produces a plastic mass that can be blown into molds, drawn into tubing, or shaped by rolling or pressing. Separation from the graphite rod is facilitated by gaseous products formed by interfacial reaction. Because the outside is sandy, the product is known as sand-surface ware. A matte finish is obtained by mechanical buffing. A glazed surface is produced by fusing the outside surface with an electric carbon arc or flame.

The Rotosil process employed by Heraeus and Heraeus-Amersil is used for the production of tubular or cylindrical shapes. It permits greater uniformity and dimensional control than the previous process. The quartz is washed in hydrofluoric acid and distilled water to remove impurities that can promote crystallization during manufacture. The sand is then placed in a rotating horizontal steel tube where it is held at the circumference by centrifugal force. A carbon arc is passed slowly down the center of the drum to fuse the sand. A modification, using open rotating molds on a vertical axis, allows formation of crucibles, beaters, and bowls.

For refractory applications, sand of moderate purity is fused by an electric arc into an ingot. The ingot is then crushed and ground to a size suitable for injection molding or slurry casting. A variety of shapes can be produced, including bricks, nozzles, and pouring tubes. After shaping, the pieces are dried slowly and then fired at 1150–1250°C for 1–4 h. The materials have a white, opaque appearance.

**Transparent Vitreous Silica.** Clear, transparent, bubble-free vitreous silica may be obtained by melting natural quartz minerals by flame or plasma vapor deposition (synthetic fused silicas), and by sol-gel processing.

*Fused Quartz.* The fused quartz glasses correspond to the Type I and Type II vitreous silicas described in Table 1. Type I silica is made by the direct melting of quartz powder using the resistance, ie, Osram process (43), or induction-heated furnaces (44). The powder is fed into the top of a tubular furnace and melted in either a molybdenum or carbon crucible surrounded by a protective inert or reducing gas. Tubing or rod can be drawn from the bottom of the crucible. Vacuum is sometimes used prior to fusion to minimize the gas content in the pore spaces and hot pressing is sometimes applied after fusion to reduce the remaining bubbles. Type II silica is formed using a process originally developed by Heraeus. Quartz powder is fed through an oxy-hydrogen flame and collected as a dense glass on a rotating fused-quartz tube (45). The glass is withdrawn slowly from the flame as the fused quartz builds up. Chlorine can be introduced during laydown of the glass to improve glass purity. The chlorine removes metal contaminants, eg, aluminum, iron, copper, zinc, titanium, and the alkali and alkali-earth metals, by forming volatile chlorides (46).

The crystalline quartz powder is treated before use to improve purity and to eliminate the formation of gaseous inclusions during fusion. The powders are first washed in mixed acids, including hydrofluoric acid, to remove surface contaminants and then heated to at least 800°C and plunged into distilled water to promote extensive microcracking. The resulting powder is well suited for vacuum melting because it melts faster and expels gaseous impurities more completely than untreated quartz crystals.

Brazil continues to be an important source of quartz powder for fused quartz manufacturers. Namibia and the Malagasy Republic are also suppliers. In the United States, large deposits of crystalline quartz exist in West Virginia, Pennsylvania, and Missouri. Suppliers as of the mid-1990s included U.S. Silica and Unimin Corporation. Alternatives to the natural quartz powder, including fumed silica, flame-hydrolyzed soot, and sol-gel-derived powder, have also been tried as feedstock for these processes (11).

Although fused-quartz production is usually carried out above the melting point of cristobalite, powder sintering at temperatures in the range of 1400–1710°C is also possible (47). To avoid cristobalite formation (devitrification) while sintering at these temperatures, the powder must be pure, especially of alkali contaminants, and the time at temperature must be kept to a minimum. Typically, the sintering process takes no >15 min in the 1400–1710°C range. The sintering is usually done in a vacuum or in a helium atmosphere to minimize bubble formation.

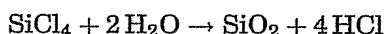
Transparent vitreous silica crucibles can be produced by firing slip-cast pieces in a vacuum or a helium atmosphere (48,49), or in helium followed by argon (50). The crucible is usually supported on a graphite form to minimize distortion.

*Synthetic Fused Silica.* Synthetic silica can be prepared from a variety of volatile silicon compounds by oxidation or hydrolysis in a flame or plasma. Type III silica is made using a flame (40,51). In the United States, the flame is typically methane–oxygen. In Europe and Japan, hydrogen–oxygen flames are preferred. Type IV silica is made with a low water, oxygen plasma (52,53). The plasma deposition process was developed as a way to produce low OH vitreous silica. In glasses made by flame hydrolysis, the OH level ranges from 800 to

1200 parts per million (ppm) depending on the flame mix. In glasses made by plasma deposition, it is typically <20 ppm.

Vitreous silicas made from chemical precursors are significantly purer than those from natural quartz powders because it is possible to purify chemical precursors to a higher degree than powders. This purity directly translates into higher uv and deep uv optical transmission of the final glass. Synthetic fused silicas can have a total metal content <200–300 ppb. Any stable, silicon-containing compound having sufficient volatility can be used as a chemical precursor (40,54). Most industrial processing uses silicon tetrachloride because it is relatively inexpensive and readily available in large quantities. Environmental concerns have, however, prompted the development of synthetic fused silica made from cyclic and chained siloxane compounds (55,56). These chlorine-free precursors do not generate HCl as a manufacturing by-product (see SILICON COMPOUNDS).

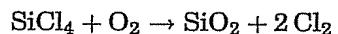
In the typical flame or vapor-phase hydrolysis process, which uses  $\text{SiCl}_4$  as the precursor, silicon tetrachloride vapor is fed into a flame using an oxygen carrier gas. Fine (<50 nm) amorphous silica particles form in the flame (57).



The water is a product of combustion of the hydrogen or methane gases. A portion of that water can also incorporate in the glass structure as  $\text{SiOH}$ .

The manufacture of vitreous silica by flame hydrolysis can be a single- or multistep process. In the single-step process, silica particles are formed and consolidated to dense glass in one operation. Consolidation takes place as the silica particles are collected on a substrate that is heated by the deposition flame. The deposition temperature is usually in excess of 1800°C. The single-step process as described here naturally yields vitreous silica that is relatively high in hydroxyl content. Further, the final material contains other combustion products depending on the flame and deposition conditions. Molecular  $\text{H}_2$ , eg, is easily incorporated in the glass using this process. In a two-step process, the silica is formed as a soot that can be collected as a powder or porous preform (low temperature deposition) and consolidated to dense glass in a separate operation. Consolidation is usually done at 1400–1700°C. The two-step process, although more involved, offers several advantages, including the ability to chemically treat the silica soot before final consolidation and to control the consolidation atmosphere. For example, high purity, low OH vitreous silica can be made by chemically drying the porous preform in chlorine (58) or  $\text{SOCl}_2$  (59) and then consolidating in a moisture-free atmosphere. This operation is a key step in the production of optical waveguide fibers, which require low OH for ir transmission, but can also be used to manufacture bulk glass (60,61).

In the plasma deposition process, silicon tetrachloride vapor is passed through an induction-coupled plasma torch using a hydrogen-free oxygen stream:



The resulting silica is deposited on a refractory substrate as a clear transparent glass.

Synthetic fused silicas with low OH levels have also been made experimentally using a CO<sub>2</sub> laser instead of the plasma torch (62,63). The glass rate of this process, however, is at least 10 times slower than the plasma approach.

Fused silica materials obtained by the various vapor-phase methods can be formed into rods, tubing, and boules. The pieces may range in size up to hundreds of kilograms. Any of these may be subsequently reworked to make a variety of useful products. Crucibles have been made from both tubing and massive pieces. Optical elements are cut from the boules and polished, and often finely annealed to control refractive index and reduce internal stress.

*Sol-Gel Processing.* Sol-gel processing is essentially a lower temperature alternative for fabricating synthetic fused silica (64–70). The starting material is either a particulate gel made by mixing fumed or colloidal silica in an appropriate liquid or a solution of a silicon alkoxide, such as tetraethylorthosilicate (TEOS) or silicon tetramethoxide, in alcohol using a controlled amount of water that hydrolyzes slowly to form a gel. After the gel is dried, it can be sintered under vacuum or in helium atmosphere to transparent vitreous silica at temperatures of 1200–1400°C. Steps are often taken to minimize the OH and chlorine content of the preforms to avoid bubble formation during sintering (71,72).

The gel approach offers processing advantages that are not available with the more conventional methods used to form synthetic fused silica. The lower firing temperatures reduce energy consumption and minimize the pickup of furnace impurities. Also, near-net-shaping is possible because the gelling procedure is not limited to any particular mold configuration. Unfortunately, the gel approach has critical drying and shrinkage problems that have thus far limited the glass sizes that can be produced. The gels, fragile structures that tend to crack during drying owing to capillary stresses, are highly porous structures that shrink linearly by up to 50% upon firing. The high shrinkage makes dimension control difficult. These problems have been attacked with limited success by increasing gel strength through gel aging, additions of silica particle fillers, etc; controlling the pore size in the gel through pH control and hydrothermal aging (73); and slower, milder drying procedures (see HYDROTHERMAL PROCESSING; SOL-GEL TECHNOLOGY). In response to these processing limitations, several hybrid processes have been proposed that use sol-gel derived powders as the feedstock for more conventional manufacturing approaches, including flame fusion and high temperature vacuum sintering (11,74).

*Flame Working and Sealing.* Flame working of vitreous silica is difficult because of its extremely high viscosity and volatility. However, this drawback is balanced by excellent resistance to thermal shock. Whereas a gas–oxygen flame is satisfactory for most manipulations, an oxy–hydrogen flame provides somewhat more energy. An oxy–acetylene flame gives even more heat, but promotes excessive volatilization.

When silica volatilizes, vapors condense on cooler areas to form a white bloom that can be removed by heat or dilute hydrofluoric acid. Because dilute hydrofluoric acid also attacks the substrate, a mild, careful treatment is required. To minimize volatilization, the temperature should be as low as possible.

Annealing of flame-worked pieces is generally not necessary because of the low thermal expansion of vitreous silica. However, massive pieces should be

Table 10. Manufacturers and Suppliers of Vitreous Silica

Company	Location
<i>United States</i>	
A. A. I. Products Inc.	Woodbridge, N.J.
Cabot Corp.	Boston, Mass.
Corning Incorporated	Corning, N.Y.
Dynasil Corp. of America	Berlin, N.J.
GE Quartz Products	Cleveland, Ohio
OSRAM-Sylvania	Exeter, N.H.
Heraeus Amersil Inc. <sup>a</sup>	Duluth, Georgia
J. P. Stevens & Co., Inc.	Greenville, S.C.
Pyromatics, Inc.	Willoughby, Ohio
Quartz Products Co. <sup>b</sup>	Louisville, Ky.
Quartz Scientific, Inc.	Fairport Harbor, Ohio
<i>Outside United States</i>	
Asahi Glass	Tokyo, Japan
Heraeus Quarzglass GmbH	Hanau, Germany
Hitachi Cable	Tokyo, Japan
Iruvisil Co., Ltd.	St. Petersburg, CIS
Fujikura	Tokyo, Japan
Mitsubishi Cable	Itami, Japan
Shin-Etsu Quartz Products Co., Ltd.	Kokai, Japan
SICO	Jena-Burgau, Germany
Sumitomo Electric Industry	Osaka, Japan
Thermal Quarz Schmelze GmbH <sup>c</sup>	Weisbaden, Germany
Thermal Syndicate, Ltd. <sup>b</sup>	Wallsend, U.K.
Toshiba Ceramics	Tokyo, Japan
TOSOH/Nippon Silica Glass	Tokyo, Japan
Quartz & Silice <sup>b</sup>	France, Holland, Italy
Westdeutsche Quarzsenschmelze GmbH <sup>c</sup>	Munchen, Germany

<sup>a</sup>Subsidiary of Heraeus Quarzglass GmbH.<sup>b</sup>Subsidiary of Saint-Gobain Group Co. Quartz Technology Division.<sup>c</sup>Subsidiary of General Electric.

and silicon wafer furniture. The principal U.S. and foreign manufacturers of vitreous silica are listed in Table 10.

## 6. Uses

**6.1. Chemical Applications.** Because of its excellent chemical durability, high purity, thermal shock resistance, and usefulness at high temperature, vitreous silica has a wide range of applications in chemical analysis and preparations. Tubing, rods, crucibles, dishes, boats, and other containers and special apparatus are available in both transparent and nontransparent varieties (120,141,142,220). Because of its inertness, vitreous silica is used as a chromatographic substrate in the form of microparticles, capillary tubing, and open columns for high resolution gas chromatography (see ANALYTICAL METHODS; CHROMATOGRAPHY) (221).

**6.2. Thermal Applications.** The protection of precious-metal thermocouples in high temperature pyrometry is an important application of vitreous

silica. Although satin tubing is usually employed, transparent tubes are superior for protecting couples when used in a reducing atmosphere (222).

Vitreous silica is used for gas- or electrically heated devices in various shapes, eg, as a tube or muffle because of its electrical resistivity, impermeability, and low expansion. In its simplest form, an electric-resistance furnace consists of a vitreous silica tube or pipe on which the resistance element is wound (see FURNACES, ELECTRIC INTRODUCTION). Because of its indifference to temperature gradients, a tubular furnace of vitreous silica may be made to operate at different temperatures at various portions of the tube, either by arrangement of the heating elements or by cooling sections of the tube with water. Vitreous silica pipes may be employed in vacuum induction and gas-fired furnaces (see VACUUM TECHNOLOGY) (223).

Radiant heaters employing resistance wire encased in vitreous silica tubes have the capability to modify the emitted radiation and furnish a higher proportion of shorter ( $1\text{--}2\ \mu\text{m}$ ) wavelengths that constitute the desirable radiations. Immersion heaters for use with acid solutions are of similar construction. An overhead heating unit consisting of a resistance wire sealed inside a vitreous silica container permits acid liquids to be concentrated or evaporated without ebullition or spattering. High efficiency radiators  $\sim 200\text{-cm}$  long have been developed for power requirements up to 6 kW. These are used as energy sources in heat exchangers (see HEAT-EXCHANGE TECHNOLOGY), high duty enamel drying equipment, polymerization processes, and copying devices (223).

Insulation having high thermal endurance has been made from vitreous silica fibers (see ABLATIVE MATERIALS). Such material forms the basis for the 30,000 insulating tiles, 125-mm thick, that protect the aluminum skin of the space shuttle. The tiles add a minimum of weight because the density of the insulation is only  $144\ \text{kg/m}^3$  ( $9\ \text{lb}/\text{ft}^3$ ), similar to balsa wood.

*Optical Applications.* Vitreous silica is ideal for many optical applications because of its excellent uv transmission, resistance to radiation darkening, optical polishing properties, and physical and chemical stability. It is used for prisms, lenses, cells, windows, and other optical components where uv transmission is critical. Cuvettes used in scatter and spectrophotometer cells are manufactured from fused silica and fused quartz because of the transmissive properties and high purity (224).

The development of high power laser systems at shorter uv wavelengths requires the transmissive and optical properties of fused silica. These high power lasers are utilized for commercial energy research and military applications. Excimer lasers are utilized in photoablation, photolithography, material processing, and medical applications. The optical beam delivery systems for these excimers can utilize fused silica lenses or optical fibers (225,226), as well as fluoride-based optics, eg,  $\text{CaF}_2$  and  $\text{MgF}_2$ .

All higher energy laser systems throughout the world utilize a significant amount of high quality fused silica. Inertial confinement research laser systems, such as the Lawrence Livermore National Laboratory (LLNL) NIF (National Ignition Facility) laser that operates at 366 nm (frequency tripled Nd-YAG laser), require fused silica for the transport and cavity spatial filter lenses, Pockel cell windows, vacuum windows, final focal lens and the debris shield (227). Inertia confinement fusion research is also underway using KrF (248-nm)

laser systems, eg, the Los Alamos Aurora and Naval Research Laboratory NIKE. These utilize a fused silica (Corning Code 7980).

**6.3. Mechanical Applications.** The volume of vitreous silica used for fibers is a very small part of the total consumption. However, some interesting and significant applications have been developed in the laboratory, particularly in the area of measurements.

The sorption balance employs 15 small vitreous silica springs enclosed in glass tubes (228). The fiber is 2 mm in diameter and the coils 1.25 cm in diameter and 5.99 cm long (see WEIGHING AND PROPORTIONING). A platinum bucket, which weighs 202 mg, contains up to 0.5-g charcoal; the balance can be read to 0.2 mg. The sorption of gases is determined over a wide range of temperatures and pressures. This type of balance has been used for density determinations, measurements of heat loss and evaporation, study of chemical reactions between gas and solid phases, and weight determination of wet tissues of plant and animal origin. The advantages of vitreous silica are its resistance to corrosion, ease of cleaning and sterilization in an enclosed tube, and absence of damping from internal friction.

Because of its low and regular thermal expansion, vitreous silica is employed in apparatus used to measure the thermal expansion of solids. A detailed account of the different methods used for this purpose has been published (229). The most common form of dilatometer utilizes a vitreous silica tube closed at the bottom and containing the test sample. A movable rod of vitreous silica, resting on the sample, actuates a dial indicator resting on the top of the rod. The assembly containing the sample is placed in a furnace, bath, or cooling chamber to attain the desired temperature.

**6.4. Lighting.** An important application of clear fused quartz is as envelop material for mercury vapor lamps (230). In addition to resistance to deformation at operating temperatures and pressures, fused quartz offers uv transmission to permit color correction. Color is corrected by coating the inside of the outer envelope of the mercury vapor lamp with phosphor. Ultraviolet light from the arc passes through the fused quartz envelope and excites the phosphor, producing a color nearer the red end of the spectrum (231). A more recent improvement is the incorporation of metal halides in the lamp (232,233).

Incandescent tungsten-halogen (F, Br, I) cycle lamps first became available in 1959 for general use. In this lamp, tungsten evaporating from the filament deposits on the envelope wall where it reacts with halogen vapor to form a volatile halide. The tungsten halide diffuses back to the filament where it dissociates to halogen vapor and tungsten. This permits a higher temperature operation, which affords higher efficiency and longer life than the conventional incandescent lamp. The wall temperature must be at least 250°C and, if possible, ~600°C. Fused quartz has been essential for this development because it is one of the few readily available transparent materials that can be used in lamp envelopes. Improvements include the internal deposition of a barrier, eg, aluminum fluoride or aluminosilicate (234,235), and reflective layers, eg, titanium silicate or zirconia (236,237). These protect the silica glass from vapor attack, slow the diffusion of deactivating impurities, and reflect heat onto the filament while transmitting visible light. These lamps are used in the illumination of airfields, sports arenas, buildings, streets, parking lots, and automobiles.

They are also used in slide and film projectors and specialized optical instruments (238,239).

**6.5. Electronic Applications.** In electronic systems, such as radar and computers, signal delay is sometimes necessary. A transducer converts electrical signals to ultrasonic elastic waves, which pass through a connecting medium to another transducer, where the waves are reconverted to electrical signals. Vitreous silica is an ideal connecting medium because it has excellent physical stability and low ultrasonic transmission losses. It transmits an ultrasonic signal almost 100,000 times more slowly than an electric signal in a wire. The vitreous silica delay line is in the form of a flat polyhedral plate. The facets of the edges of this plate are ground to a predetermined angle with great precision. The transducer is fastened to one of these facets. The plates may be designed for path lengths of 4 cm to nearly 12 m, giving delay times for shear waves of 10–3000  $\mu$ s (240).

By far the most significant electronic application, and perhaps the highest volume application for vitreous silica, is in semiconductors (qv). This association began with silicon wafer technology, where vitreous silica was the principal high purity material for crucibles for silicon crystal growth. Both opaque sintered and transparent vitreous silica from tubing or boules are used. Crucible sizes have been increasing in response to the demand for ever-larger silicon wafers.

Vitreous silica tubes are used for the subsequent high temperature diffusion, doping, and epitaxial growth treatments performed on wafers destined for large-scale integrated circuits. Once again, the high purity of certain grades of vitreous silica, along with its high thermal endurance, make it the material of choice for diffusion tubes, wafer holders, boats, and associated hardware. Quartz manufacturers continue to push for higher purity, ie, alkali content in tubing approaching <1 ppm. The thermal endurance of the tubes may be prolonged by causing some surface crystallization; the increased rigidity prevents sagging (141). Diffusion-resistant barrier coatings have also been used (241,242). In addition to silicon wafers, many other high temperature, high purity solid-state reactions are performed in vitreous silica vessels, including crystal growth, zone refining, and the preparation of gallium and indium arsenides, as well as germanium and silicon optical materials.

Thin films (qv) of vitreous silica have been used extensively in semiconductor technology. These serve as insulating layers between conductor stripes and a semiconductor surface in integrated circuits, and as a surface passivation material in planar diodes, transistors, and injection lasers. They are also used for diffusion masking, as etchant surfaces, and for encapsulation and protection of completed electronic devices. Thin films serve an important function in multi-layer conductor insulation technology where a variety of conducting paths are deposited in overlay patterns and insulating layers are required for separation.

Thin vitreous silica films are usually formed by vapor deposition or r-f sputtering (see THIN FILMS, FILM-DEPOSITION TECHNIQUES). Vapor deposition is generally effected by the pyrolytic decomposition of tetraethoxysilane or another alkoxy silane. Silica has been most extensively used in r-f sputtering of dielectric films, which are of very high quality.

Large-scale and very large-scale integration (VLSI) of electronic circuits requires the photoreduction of complex conductor and insulator patterns,

which are reproduced on semiconductor devices by various photoresist processes. Vitreous silica is frequently used for the photomask substrate, ie, the transparent substrate for the image mask that contains the basis for conduction or insulator patterns. Because of the extremely high dimensional tolerances of VLSI, vitreous silica is a natural choice for the substrate. Its uv transmission properties allow fast exposure of the photoresists, and its very low thermal expansion prevents pattern distortions owing to temperature gradients encountered during processing. Perfectly flat and inclusion-free material is required (243). Another application for fused silica in the semiconductor field is as optical elements in microlithographic systems. In order to obtain smaller features on computer chips, ie, increasing the memory capacity, photolithographic stepper and scanner systems are moving to shorter wavelengths. Vitreous silica is used to make the excimer-based deep uv (248 and 193 nm) lithographic lens systems because of its superior uv transmission and radiation resistance characteristics. These lens systems are used to manufacture 256-Mb dynamic random-access memory computer chips(DRAM) (226) and increasingly higher density NAND and NOR flash memory chips, whose growth rate is currently (2006) >30%/year. The refinement of silica properties for use at 193nm (particularly radiation resistance) is particularly important because 193-nm technology is being optimized further than previously thought possible. These systems are now being extended to manufacture circuit dimensions of <100 nm; this size was once intended to be manufactured using 157-nm lithography or other future technologies. In addition, titanium-doped silica (eg, Corning Incorporated ULE) is being explored for its use in extreme uv (13nm) lithography. Mirrors made from materials such as this offer the lultralow thermal expansion required for producing features in the 20-nm range.

**6.6. Space and Astronomy.** Vitreous silica is used in several space-based applications because of static fatigue (slow crack growth), thermal stability, and radiation resistance. Every U.S. space vehicle having service personnel, including Mercury, Gemini, Apollo, and space shuttle vehicles, has been equipped with windows made of high optical-quality vitreous silica (Corning Code 7940 or 7980) in order to have the clarity needed for visual, photographic, and television-based observations. The space shuttle utilizes triple-layer windows that have outer and central panes of vitreous silica with a tempered aluminosilicate inner pane. The outer pane is thinner for thermal endurance, whereas the two inner panes are thicker to supply strength (244).

The ability of vitreous silica to withstand dimensional changes with changing temperature has made it ideal for mirror blanks of telescopes (245–247). Vitreous silica is used in both space- and ground-based mirror applications because of the thermal stability and the ability to polish to ultrasMOOTH surface. The mirrors for space-based applications are fabricated by fusion-sealing struts into a honeycomb structure of vitreous silica, which is then fused or bonded with expansion-matching materials to top (face plate) and bottom (backer) plates. Weight reductions of up to 93%, relative to the weight of an equivalent-sized solid glass blank, can be achieved using these sandwich structures.

An ultralow expansion (ULE) vitreous silica (ULE-Corning Code 7972) can be manufactured by doping the silica with a 7.5% titanium dioxide (148,244). The sonic velocity and coefficient of thermal expansion (CTE) are directly

related to the titanium concentration. This material was used to manufacture the 2.4 m dia lightweight mirror blank for the Hubble telescope and the 8.3-m mirror blank for the ground-based Japanese National Large Telescope (JNLT). The JNLT piece, the largest mirror blank in the world, was manufactured by hex-sealing titanium-doped vitreous silica pieces into a solid glass mirror weighing >30 t (248).

Space-based solar cells are covered with a very thin layer of vitreous silica to protect against the damaging environment of space such as atomic oxygen, micrometeorites, and radiation effects. Because the silica is transparent to damaging uv radiation, it is normally coated with a uv-reflective thin film (see SOLAR ENERGY).

The Topex oceanographic satellite used a laser-based retroreflector array for positioning. The retroreflectors were manufactured from Corning Code 7958 fused silica, a sol-gel-derived low water vitreous silica material (249).

**6.7. Optical Fibers.** Pure and doped fused silica fibers have replaced copper lines in the telecommunication area. Fused silica fibers are used in laser surgery, optical sensor application, and laser welding (see SENSORS). Optical-fiber-tethered weapons, eg, fiber-optics-guided (FOG) missiles are another potential application for fused silica (250,251). Silica glass has also been used to fabricate microstructured air-core photonic band gap fibers (252). These fibers consist of an air core surrounded by a periodic lattice of air holes in glass. Light guidance in these fibers is based on the principle of interference to reflect radiation. The fibers can be made in long lengths, starting with a "stack-and-draw" process (253,254). In this process, a preform of silica capillaries is stacked into the desired lattice. Subsequent drawing processes reduce the pre-form to fiber dimensions (typically for telecommunications applications the final fiber diameter is 120  $\mu$ ). The lattice spacing of the air holes is on the order of 3–5  $\mu$  for the telecommunications applications; glass thickness between the air holes is on the order of hundreds of nanometers. Much of the success of silica in these applications can be related to its wide working range. (see FIBER OPTICS).

**6.8. Other Uses.** Vitreous silica also has applications in the form of powders, fibers, wool, and chips (255). The powder may be used as an inert filler or as a coating material in the investment-casting industry for the lost-wax process. Chips are used as an inert substrate in certain chemical process applications. Vitreous silica wool or fiber is an excellent insulation or packing material. Complex shapes rendered in extruded or sintered vitreous silica are used to produce precisely shaped holes, tunnels, cavities, and passages in investment-cast metal parts (see also REFRACTORIES). The vitreous silica shapes are chemically compatible with most alloys and dimensionally stable at casting temperatures. They give smooth internal surfaces to the cast pieces. The cooled casting is subsequently treated in hot caustic solutions to remove the silica core. Sandblasting may also be used. Internal features such as long holes and cooling passages for turbine rotors, which would be impossible to fabricate by drilling or machining, are obtained routinely (256).

Antireflective (AR) coatings are required on optics to reduce the reflective surface losses. Vitreous silica coatings in the form of porous or multilayer films are used extensively in this application. Antireflective coatings have been